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None

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(54) **Fire resistant in organically bonded laminates**

(57) Laminates constructed using layers of reinforcing and/or non-reinforcing materials bonded by at least one layer of a composition of a metal oxide, calcium silicate and phosphoric acid that provides water-resistant phosphate ceramic materials. The products are fire-resistant and intumescent when exposed to heat or direct flame, and produce little or no smoke, while being tough, durable and capable of a decorative and pleasing appearance.

A specification referred to in the application and appended to it is not included in the print but is available for inspection in accordance with the provisions of Section 118(1).

achieve this result include those disclosed in U.S. Patent No. 4,375,516. That patent discloses that compositions comprising calcium silicate, phosphoric acid and a metal oxide selected from aluminium oxide, magnesium oxide, calcium oxide and zinc oxide, and the hydrates thereof, would react to provide water-resistant phosphate materials; however, it has now been discovered that other metal oxides can also provide water-resistant phosphate materials. Accordingly, there may be used in making the laminates of the present invention any composition comprising a metal oxide, calcium silicate and phosphoric acid, provided that it reacts to provide a water-resistant material, and it will be understood that the term "metal oxide" includes a hydrated metal oxide.

These compositions are coated, preferably in relatively thin layers on the order of *ca* 1-20 mils (*ca* 0.025 to 0.5 mm) thick, onto the surface of a layer material which may be a reinforcing or a non-reinforcing material. The compositions may be applied at normal consistency, or they may be applied as mechanically frothed foams. Where very thin coatings are desired or where lighter-weight laminates are desired, the latter technique is preferred because the foam may be applied at a thickness of *ca* 1 mil (0.025 mm), after which the thickness is reduced to a thinner dimension as the foam collapses. Further, the bonding composition may be applied, for example in a discontinuous manner, to a portion or portions only of the layer material. Accordingly, the term "layer" of bonding material is intended to encompass applications in which this material is deposited either in a uniform or in a non-uniform manner, and in a continuous or discontinuous manner.

After applying the bonding composition, the coated material may then be allowed to cure, or it may be covered with a second layer of the same or a different layer material and then allowed to cure. Curing may be achieved under ambient conditions; however, where more dense products are desired, curing may be effected under pressure. In addition, heat may also be applied during curing to accelerate the curing process.

A variety of materials may be used to provide the laminates according to the invention. For example, kraft paper, paper towel, cheese cloth, woven, non-woven, and chopped glass mats, woven non-woven and chopped synthetic materials, for example, polyester or nylon, chopped fibers or various materials, mineral wool, wire mesh and other well-known materials may be used alone or in combination as layer materials. In addition to reinforcing materials, non-reinforcing materials, for example, cementitious materials, may also be used although, in most instances, products which are more rigid in character result.

Particularly effective reinforcing materials for use in combination with the phosphate bonding materials disclosed herein are materials which are disclosed in copending U.S. Application Serial No. 588,576 (European Patent Application No. , Serial No.), and also in U.S. Patent No. 4,239,519 and patents related thereto, the contents of which are incorporated herein by reference. These references, when considered collectively, disclose a class of material which is referred to herein as "synthetic mica" materials. In essence, they are asbestos-free papers or sheets which are derived from silicate gels by cation exchange reactions. Materials of this type are known to be relatively unaffected by high temperatures, yet they tend to have good flexibility.

Laminated structures comprising layers of the phosphate bonding materials and synthetic mica sheets have shown remarkable characteristics. For example, when such composites were exposed to direct flame, they not only proved to be fire-resistant and relatively smoke-free, but they also demonstrated intumescent properties. That is, the exposure of one surface of the structure to direct flame was observed to cause an apparent internal delamination of the structure, resulting in the production of air spaces. Such air spaces are insulative in nature, and dramatic heat differentials have been noted between two sides of a structure tested in this manner. For example, although one side of a relatively thin structure on the order of 0.06 in. (1.5 mm) in thickness was exposed to direct flame at a temperature of about 2050°F (1120°C) for 1 minute, internal swelling occurred and the temperature on the opposite side of the structure was less than 600°F (315°C).

This phenomenon is not restricted to laminates constructed using synthetic mica materials. For example, laminates comprising kraft paper also exhibit intumescent properties, and large temperature differentials have been noted for these laminates when tested as described above. The reason why delamination occurs is not clearly understood, although it is believed to be associated at least in part with water contained within the structure.

In addition to intumescent laminates, heat conducting laminates may also be produced by including wire screen as one of the layers. Laminates of this type are effective in conducting heat away from the point of application; thus, these materials are useful for example as heat-conducting gaskets.

The thickness of the laminates produced according to the present invention may vary widely. At the desire of the artisan, structure thickness may be varied from very thin (e.g. 0.03 in. or 0.076 mm) to very thick (e.g., 0.5 in. (12.5 mm) or more). Laminated structures have been produced comprising as few as one layer of one reinforcing material and one layer of phosphate bonding material, or as many as 37 layers of reinforcing layers and 36 layers of phosphate bonding material. This illustration, however, is not intended to limit the number of layers which could be included in a laminate. Furthermore, there is no necessity to restrict the reinforcing materials used in making the laminated structure to a single type, and combinations of reinforcing materials may be used to advantage.

Example 6

A phosphate bonding material was prepared comprising the following components:

	Components	Weight (grams)	
5			5
	Al ₂ O ₃ ·3H ₂ O	18.0	
	MgO	8.0	
	Talc	16.0	
10	75% H ₃ PO ₄ (53.0% P ₂ O ₅)	108.0	10
	H ₃ BO ₃	4.0	
	CaSiO ₃	100.0	
	H ₂ O	18.0	

15 The reaction solution was prepared by mixing the phosphoric acid, the water, and the alumina trihydrate and stirring until a clear solution was obtained. The boric acid was added to the resulting warm solution and stirred. After this solution has become clear, the reaction solution was chilled to about 35-39°F (2 to 4°C).

To the 148 grams of cold liquid was added, with vigorous stirring, the 124 grams of remaining dry components which had been mixed to provide a uniform material. The resulting mixture was stirred until it had become homogeneous, and it was then placed in an ice bath to prolong the liquid consistency; i.e., to delay the interaction of the components. The pot life of this material could be varied from about 30 seconds to about 7 minutes, depending on the capability of controlling the exothermic reaction temperature in the ice bath.

A synthetic mica sheet was prepared from the following components essentially as described in the aforementioned compounding application:

	Component	Weight (grams)	
30			30
	Magnesium fluorhectorite	100.0	
	Bleached redwood cellulose	10.0	
	1/8" (3 mm) DE glass fibers	5.0	
	Polymin P flocculating agent	0.075	
	Hydraid 777 flocculating agent	0.037	
35	Water	—	35

The bleached redwood cellulose was dispersed in water by means of a hydropulper and was refined in a Jordan Refiner until a consistency of 500 (Canadian Freeness) was obtained. The refined pulp was transferred to a large, open-head tank and was slurried with the glass fibers. After charging the required amount of water into the tank to get a content of 1.3% solids, the magnesium fluorhectorite floc was added and the mixture was stirred until it was homogeneous. The Polymin P and Hydraid 777 were then added and the composition was immediately flowed onto the forming screen of a Fourdrinier machine. After removing most of the water, the mat was subjected to vacuum in a series of vacuum presses. Residual water was then removed by passing the synthetic mica mat over a heated drum.

45 A thin coating of the above phosphate bonding material (I) was brushed at a thickness of approximately 10 mils (0.25 mm) onto the surface of a synthetic mica sheet (S). A piece of microlith glass sheet (G), designated SH20/I from Glaswerk Schuller GmbH, was immediately placed in the bonding material and saturated, and the second synthetic mica sheet was placed on top of the glass layer. The assembled materials were placed in a press between glass surfaces and pressed under 250 psi (1.72 MPa) pressure for five minutes at 170°F (77°C). After pressing was complete, the pressed composite was conditioned at 170°F (77°C) for several additional minutes to remove water, giving a product which was strong and flexible.

It was noted that, because of the porous nature of the glass sheet, the bonding material did not have to be applied on both sides of the glass sheet. The bonding material was capable of passing through (saturating) the glass layer under pressure such that both contiguous layers of synthetic mica could be bonded to the glass through a single application of bonding material. In this and the following examples the saturation is indicated by (GI) or (IG). Accordingly, the structure of this example had the laminate order S(IG)S.

Example 7

A process similar to that of Example 6 was repeated except that glass sheets constituted the exterior layers and the composite material had the structure (GI)S(IG). The glass sheets were bonded with the phosphate bonding material to the single internal layer of synthetic mica sheet by placing the composite in a press that was equipped with shallowly patterned embossing plates. The plates provided a fine texture in a desired design to the surface of the laminate.

The metric equivalents of the above results are as follows:

	<i>Sample</i>	<i>MOR (MPa)</i>	<i>MOE (GPa)</i>	
5	9I	11.81	2.23	5
	9J	15.60	2.65	
	9K	16.24	3.25	

Example 10

10 This example will illustrate the results when various samples were heated with a propane torch as described in Example 3. The results are indicated below for laminates having various components and structural arrangements. 10

Heating caused noticeable changes to the laminates, and these changes became more pronounced as the number of layers increased. For example, when heat was applied to a single synthetic mica sheet, only a small expansion of the sheet was seen. However, when two or more synthetic mica and phosphate bonding layers (with or without glass reinforcing) were utilized, blistering became more pronounced. The effect with the thicker samples, as shown below, was to provide good insulative effects. The table indicates the increase in thickness which was induced in each sample by the heating. 15

Samples were constructed of layers of SH 20/I glass sheet and/or synthetic mica bonded together with phosphate bonding material substantially as described in Example 9. The resulting laminates were unembossed. They were designated as Samples 10A through 10H and the "Structure" column lists the laminar sequence from top to bottom. 20

			<i>Thickness Change (inch)</i>			
25	<i>Sample</i>	<i>Structure</i>	<i>Initial</i>	<i>Final</i>	<i>Increase</i>	25
	10A	S	0.027	0.038	0.011	
	10B	ISI	0.034	0.125	0.091	
30	10C	(GI)S(IG)	0.037	0.130	0.093	30
	10D	ISISI	0.055	0.150	0.095	
	10E	(GI)S(GI)S(IG)	0.063	0.173	0.110	
	10F	ISISISI	0.073	0.194	0.121	
	10G	(GI)S(GI)SIS(IG)	0.085	0.210	0.125	
35	10H	(GI)S(GI)S(GI)S	0.084	0.250	0.166	35

The metric equivalents of the above results are as follows:

			<i>Thickness Change (mm)</i>			
40	<i>Sample</i>	<i>Initial</i>	<i>Final</i>	<i>Increase</i>		40
	10A	0.69	0.97	0.28		
	10B	0.86	3.17	2.31		
45	10C	0.94	3.30	2.36		45
	10D	1.40	3.81	2.41		
	10E	1.60	4.39	2.79		
	10F	1.86	4.93	3.07		
	10G	2.16	5.33	3.17		
50	10H	2.13	6.35	4.22		50

The temperatures in °C for the above results are as follows:

		<i>Temperatures (°F) as Indicated Time Intervals (seconds)</i>					
5	Sample	15	30	60	120	180	5
10	10A	1184	1193	1202	—	—	10
		547	588	597	—	—	
		637	605	605	—	—	
15	10B	1202	1217	1226	—	—	15
		457	556	551	—	—	
		745	661	675	—	—	
20	10C	1246	1276	1268	1255	1262	20
		234	573	573	579	576	
		1012	703	695	676	686	
25	10D	1016	1092	1102	1114	1126	25
		84	173	423	463	465	
		932	919	679	651	661	
30	10E	1036	1117	1117	1133	1137	30
		71	114	289	391	402	
		965	1003	828	742	735	
35	10F	1127	1152	1183	1200	1191	35
		82	93	185	379	386	
		1045	1059	998	821	805	
40	10G	1194	1215	1213	1234	1239	40
		76	82	138	348	364	
		1118	1132	1075	886	875	
45	10H	1122	1109	1134	1176	1186	45
		70	80	105	307	328	
		1052	1029	1029	869	858	

40 These results illustrate that heating causes the laminates to swell, thereby exhibiting intumescent properties. 40

Example 11

The procedure as set forth in Example 6 was repeated using synthetic mica, Schuller 20/l glass scrim, Burlington No. 1653 Lenoweave (16 × 8) glass scrim (abbreviated "B") and/or galvanized iron wire window screen (W) having 14 strands v. 17 strands per square inch (5.5 × 6.7 per sq. cm). The following samples were prepared:

	Sample	Structure	
50	11A	SIS	50
	11B	ISI	
	11C	S(IG)S	
	11D	(GI)S(IG)	
	11E	S(IB)S	
55	11F	S(IW)S	55

The products were tested for tensile strength and also for flexibility. Tensile strengths were determined essentially according to ASTM F-152 using Type 1 specimen sizes on an Instron tensile tester at 1 in./min (25.4 mm/min) crosshead speed and a chart speed of 1 in/min; however, the samples were not preconditioned. The samples were cut in a 1/2-inch (12.7 mm) dumbbell shape, with the exception of sample 11F which was cut in a 1-in. (25.4 mm) dumbbell shape.

Laminate C was prepared using galvanized iron wire as described in Example 11 whereas Laminate B was prepared to contain comparable copper wire. Laminate A, which contained no wire, was prepared as a control. The following temperatures were recorded.

5

Temperatures Recorded

5

	Time (min.)	TC 1			TC 2			TC 3			
		A	B	C	A	B	C	A	B	C	
10	0	80	80	78	81	80	78	81	81	79	10
	3	1989	1892	1911	166	191	210	99	101	96	
	10	1920	1865	1919	161	219	255	100	108	108	
	15	1861	1877	1871	200	237	261	102	110	111	
15		TC 4			TC 5			TC 6			15
		A	B	C	A	B	C	A	B	C	
20	0	81	81	79	81	81	79	81	80	78	20
	3	94	95	89	90	92	86	116	156	144	
	10	95	99	96	91	94	91	116	163	168	
	15	96	100	98	92	95	93	121	172	169	

The temperatures in °C for the above results are as follows:

25	Time (min.)	TC 1			TC 2			TC 3			25
		A	B	C	A	B	C	A	B	C	
30	0	27	27	26	27	27	26	27	27	26	30
	3	1087	1033	1044	74	88	99	37	38	36	
	10	1049	1018	1049	72	104	124	38	42	42	
	15	1016	1025	1022	93	114	127	39	43	44	
35	Time (min.)	TC 4			TC 5			TC 6			35
		A	B	C	A	B	C	A	B	C	
40	0	27	27	26	27	27	26	27	27	26	40
	3	34	35	32	32	33	30	47	69	62	
	10	35	37	36	33	34	33	47	73	76	
	15	36	38	37	33	35	34	49	78	76	

These results indicate that a laminated screen will assist in dissipating the heat from the point of application, and that copper wire will dissipate the heat more efficiently than will galvanized iron wire. In addition, by comparing the results for TC5 and TC6, it is seen that heat is more efficiently conducted in a wire direction as opposed to an oblique direction.

Example 13

This example will illustrate the preparation of a sample which is not cured under heat and pressure. A 6-mil coating of the bonding composition described in Example 1 (about 125 g) was applied to a 12 in. × 12 in. (approx 300 × 300 mm) piece of 2.5X-SM Modiglass scrim, and a second piece of scrim was placed on top of the coating. The layered material was briefly compressed to drive the bonding composition into the respective scrim layers and the composite was allowed to cure under ambient conditions. Curing was effected in about 5 minutes.

Example 14

This example will illustrate the application of a foamed bonding composition to a layer of scrim. The bonding composition was prepared as described in Example 1 and mixed for about 25 seconds. To the mixed material (268 g) was added 10.1 g (3.8%) of Millifoam surfactant from Onyx Chemical Co. and the foam was produced by mechanically mixing with an air stirrer for 40 seconds. A 3-mil (0.076 mm) coating was applied to both surfaces of a 12 in. × 12 in. (about 300mm square) piece of 7.5X-SM Modiglass scrim, the total application by weight being about 82g. The coated scrim was pressed for 25 seconds at 180°F (82°C) to give a cured sheet.

26. The invention as claimed in any one of claims 14 to 25 hereof wherein at least one of said layer materials is a wire mesh layer material.
27. A process as claimed in claim 14, carried out substantially as described in any one of the numbered samples herein.
- 5 28. A laminate comprising at least one first layer bonded to at least one second layer by a water-resistant phosphate bonding material obtainable by the reaction of a composition comprising a metal oxide, calcium silicate and phosphoric acid. 5
29. A laminate as claimed in claim 28, wherein the bonding material is obtained by the reaction of the specified composition.
- 10 30. A laminate as claimed in claim 28 or claim 29, which also comprises a layer that is permeated by the phosphate bonding material. 10
31. A laminate as claimed in claim 30, wherein the permeated layer is a glass fibre layer.
32. A laminate as claimed in any one of claims 28 to 31, wherein said first and second layers are of the same material.
- 15 33. A laminate as claimed in claim 32, which contains several such layers. 15
34. A laminate as claimed in claim 33, wherein said layers are of a synthetic mica.
35. A laminate as claimed in any one of claims 28 to 31, wherein the material of at least one first layer differs from that of at least one second layer.
36. A laminate as claimed in claim 35, which comprises several such layers.
- 20 37. A laminate as claimed in claim 36, wherein the layers are of at least three different materials. 20
38. Any new feature or combination of features hereinbefore described.

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